

Measurement of the Acidity and Fine-control of the Pore-opening Size of Zeolites

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Abstract: Zeolite has the fine property of strong acidity and micro porosity, with which active and selective catalysts are developed. Our studies on zeolites, measurement of the acidity using ammonia temperature programmed desorption and fine control of the pore-opening size by chemical vapor deposition of silica, are reviewed.

Key Words: Zeolite catalyst, Acidity, Silica CVD

1. Introduction

It is my proposal as Editor that the professor belonging to the Faculty of Engineering summarizes his/her study upon his/her retirement, and submits it to the Research Activity Report. Because this is not the duty, we can select either to write or not to write the review. I am not sure the statics in detail, however more than 50 % of the retired professor seems to accept an invitation of the review submission. The submitted review is uploaded to the homepage of the Graduate School automatically, and therefore everybody can read the review freely. I think, therefore, that the submission of the review to the Graduate School of Engineering is, more or less, effective to make everybody known of our research activity in Tottori University. Google and Yahoo search engines probably will find the research activity uploaded in our home-page.

I want to review my studies on zeolite catalysts, because these are my most important studies carried out in this University as well as in Nagoya University [1]. However, the review on these studies is not new at all, because I had a lot of chance to summarize these investigations in various journals of the academic society. Therefore, I want to report our research activity which is strongly associated with the student activity. Some of them are thus personal reports which were not written in the published paper. This is consisted of two parts; first, zeolite acidity, and second, chemical vapor deposition of silica. The former part has already been published in Chonnam National University, Korea, because it was written upon request by Prof. Dr. Jong-Ho Kim who is used to

belong to our department.

2. Measurement of the acidity

2.1 Number of the acid site

Acidity of zeolite is created by an Al atom incorporated in the zeolite framework, and the acid strength is governed by the structure of the acid site consisting of Si, Al and O atoms. Number of the acid site is relatively easy to know the significance. The *h*-peak (high temperature peak) of the ammonia TPD tells us the number of ammonia adsorbed on the acid sites. However, in the usual conditions, the number of acid site is limited due to the spatial requirement. It is interesting to know the number of acid site on the Y zeolite, because it is limited by the surface concentration. One day, a student (Kageyama kun) reported me his experimental result of the Y zeolite acidity. I surprised to see his experimental result because the number of acid site was too large to be expected. Usually, number of the acid site is less than 1.5 mol kg^{-1} of the zeolite. If the number of the acid site is greater than this value, usually something is wrong.

Ammonia TPD experiment is easy to do in my laboratory, because everybody depends on the automatic apparatus. They measure the amount of sample and installed it in the TPD cell. After the sample is set in the apparatus, they have nothing to do, and next day the experimental result is shown on the computer desk. Therefore, nobody has the mistake of the experiment. What is the reason of the too large experimental finding? Because he measured the acidity of the ammonium Y zeolite was the reason. He did not know a precise procedure of the experi-

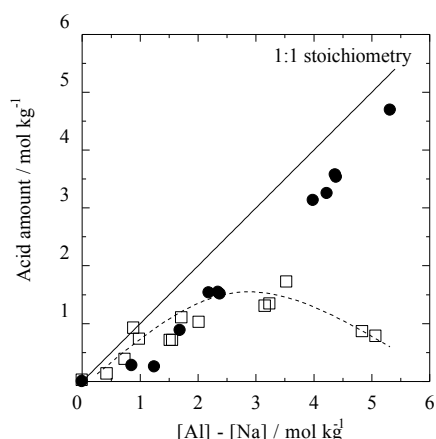


Fig. 1. Number of the acid site against the Al-Na concentration on *in situ* (●) and *ex situ* (□) prepared Y zeolites.

ment of zeolite, because he was an undergraduate student and studied the zeolite for just a few months. However, his mistake told us an important character of the zeolite acidity. Usually, we prepare the proton type zeolite by removing ammonia from the ammonium type zeolite at such a high temperature as 773 K. After the treated sample is stored in a sample bottle or exposed to the atmosphere, the experiment of the ammonia TPD is carried out. However, Kageyama kun skipped the pretreatment of the sample. From the observation, we understand that Y zeolite has shown the solid acidity due to the included Al atom even when the number of acid site is greater than 1.5 mol kg^{-1} , as far as it is unexposed to the atmosphere. We named such a prepared zeolite, *in situ* prepared Y zeolite, which is discriminated from the *ex situ* (usually) prepared zeolite. Figure 1 shows the experimental observations of the solid acidities of *in situ* and *ex situ* prepared Y zeolites [2]. *In situ* prepared Y zeolite shows the acidity which almost agrees with the number of Al up to 5 mol kg^{-1} of the framework concentration. However, the *ex situ* prepared Y zeolite shows the number of acid site which is less than 1.5 mol kg^{-1} , and the volcano-shape relation between the numbers of acid site and of Al concentration was observed. Too many atoms of Al do not show the solid acidity. From the observation, we can understand that the acid sites are collapsed when too many sites are condensed in a limited surface.

Because the specific surface area of zeolite is about

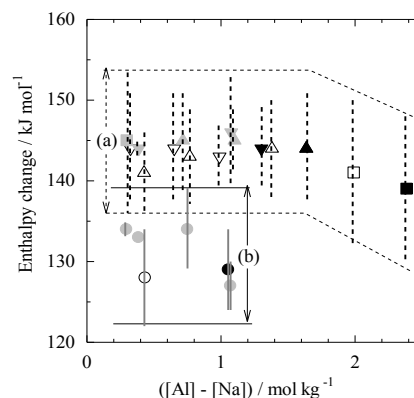


Fig. 2. ΔH as a parameter of the acid strength against the Al-Na concentration on H-mordenite (a) anZSM-5 (b).

$400 \text{ m}^2 \text{ g}^{-1}$, the maximum surface concentration of the acid site is *ca.* 2 nm^{-2} . In other words, the surface concentration of the acid site does not exceed 2 nm^{-2} . Acid sites do not exist when the surface concentration is over 2 nm^{-2} . On the highly condensed conditions, the acid sites interact mutually to destroy the site each other, *i.e.*, a spontaneous collapse of the acid site is expected. It is further proved by an experiment that water (humidity) helps to break the acid sites. Therefore, we named it a *maximum* surface concentration of the acid site. This is an important observation of the character of the acid site.

The concept of the maximum surface concentration of the acid site is an idea applicable also to the metal oxide monolayer catalysts. Vanadium, molybdenum, tungsten, and sulfated anion oxides loaded on tin, zirconium, and titanium oxides show the solid acidity of which the surface concentration do not exceed the value of *ca.* 2 nm^{-2} . Therefore, this value is useful to study the solid acidity.

2.2 Strength of the acid site

On the other hand, the concept of strength is not easy to understand. The most simple and incorrect idea is the strength measured from the temperature of the ammonia desorption. It looks like correct, but contains a serious mistake. Temperature of the ammonia desorption is influenced strongly by the experimental conditions as well as by the number of the acid site. It is not difficult to find the incorrect ex-

planations of the strength of acid sites even in the famous international journal. So many papers report the strength just by measuring the temperature of the ammonia desorption, but these are not correct.

We first observed that the temperature of ammonia desorption was influenced by the contact time of the carrier gas, W/F, when we studied the ammonia TPD in the occasion of the project of the reference catalyst, catalysis society of Japan. Temperature shifted to high with increasing the W/F by about 200 K. Such a large shift of the temperature was caused by changing the contact time of the carrier gas largely. Usually, it is difficult for a single researcher to change the W/F so largely, because the apparatus does not allow the experiments.

After many studies had been carried out, we arrived at the conclusion of a correct understanding of the ammonia TPD experiment. Equilibrium is kept always in the TPD experiment between ammonia molecules on the surface of zeolite and in the gas phase, and a small portion of ammonia molecules is desorbed to show the profile of desorption, *i.e.*, ammonia TPD.

Thermodynamics and material balance of the ammonia desorption provide us with a simple equation of the ammonia TPD shown below, *i.e.*,

$$C_g = -\frac{\beta A_0 W}{F} \frac{d\theta}{dT} = \frac{\theta}{1-\theta} \frac{P^0}{RT} \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \quad (1)$$

where θ , β , W , F , P^0 , R , and T are coverage by ammonia, ramp rate of the temperature elevation, weight of the zeolite, flow rate of the carrier, pressure at standard conditions, gas constant, and temperature. A_0 is the number of acid site, and ΔH and ΔS are changes of enthalpy and entropy upon the ammonia desorption. C_g is the concentration of ammonia in the gas phase, and this equation shows that C_g changes with the rate of decrease of θ with T , which is exactly the same as ammonia TPD profile.

The most important and fundamental observation of the TPD experiment is a constant ΔS independent of the zeolite species. Entropy increases upon desorption (phase transformation) and then mixing with helium carrier gas (mixing). The change of entropy upon mixing with helium carrier is calculated from the concentration of ammonia in the gas phase. ΔS upon desorption can be therefore calculated from the experimentally measured value. Finally, ΔS upon desorption is found to be ca. $95 \text{ J K}^{-1} \text{ mol}^{-1}$, which is

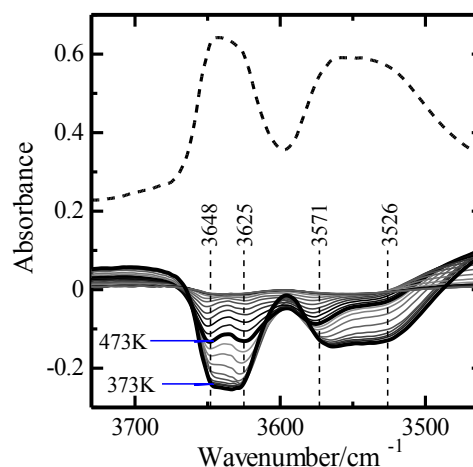


Fig. 3. An enlarged portion of the difference spectra in the region of the Brønsted OH measured by the IRMS-TPD of ammonia on H-Y zeolite: dotted line shows the reference spectrum before the adsorption of ammonia and solid lines show the difference spectra after the adsorption of ammonia.

very similar to the ΔS upon vaporization of liquid ammonia. This means that the change of entropy upon desorption is due to the change of translational energy of ammonia molecule, which supports the theoretical consideration of the ammonia TPD. A constant value of the ΔS gives us the strict background to confirm the validity of derived equation of ammonia TPD. In the laboratory, the ammonia TPD profile is calculated with the Microsoft Excel based on the above equation with a constant ΔS and assumed ΔH in order to simulate the experimentally observed one. Figure 2 shows thus determined ΔH for zeolites mordenite and ZSM-5 with different concentrations of acid sites. The measured ΔH as a parameter of the acid site strength depends on the zeolite crystal structure independent of the concentration of Al. This conclusion about the strength of acidity led to further investigation on the acidity and structure of zeolites.

2.3 Combined study on the zeolite acidity

Ammonia TPD has a serious drawback, because no information is provided for the structure of acid site.

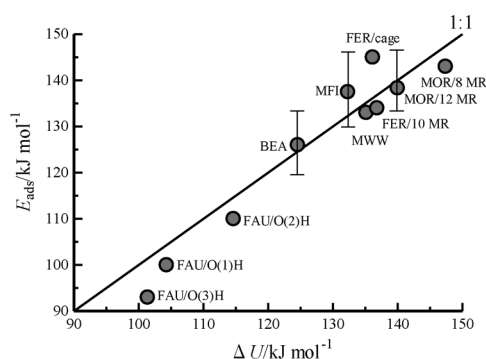


Fig. 4. Correlation between E_{ads} , DFT calculated energy for ammonia adsorption on the Brønsted OH sites and ΔU measured by IRMS-TPD. The value of E was calculated under the periodic boundary conditions of zeolites FAU, BEA, MOR, and CHA. Change of the internal energy for ammonia adsorption ΔU was corrected from ΔH due to the equation $\Delta H = \Delta U + RT$.

It is impossible with usual ammonia TPD to discriminate between Brønsted and Lewis acidities. In order to overcome the drawback, we proposed a method of IRMS-TPD experiment. In this experiment, infrared spectroscopy (IR) is measured simultaneously with the mass spectroscopy (MS). Thermal changes of not only ammonia in the gas phase but also ammonia species on the surface can be measured with this method. Ammonia adsorbed species is identified from the IR observation, and therefore Brønsted and Lewis acid sites can be discriminated. It is possible to measure the site of Brønsted OH independently, when more than two kinds of the site are observed. Thus, individual measurements of number and strength of the acid site becomes possible.

ΔH values as a parameter of the acid strength are now measured for each Brønsted OH on the zeolite, when they are discriminated. The precisely measurements of the ΔH for the Brønsted OH becomes possible by the advancement of the IRMS-TPD measurements. Interesting example of the IRMS-TPD experiment is the measurement on the Y zeolite acidity. Y zeolite has the unique property of the acid sites, because all T site are equivalent. In other words, there is only one kind of the T site. Four oxygen atoms surround the T -site in a tetrahedral configuration. Therefore, there are only four kinds of the Brønsted OH. However, a neutron diffraction

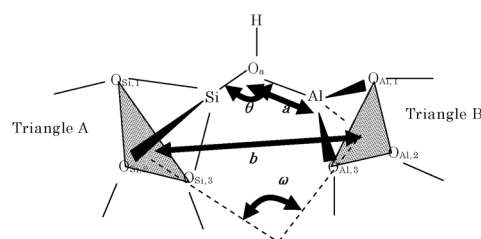


Fig. 5. A Brønsted OH cluster model surrounded by two triangles A and B with parameters of distance a , b and angle ω , θ .

study did not detect one of the four Brønsted OH sites. Experimentally, we can find four kinds of Brønsted OH, as shown in Figure 3 [3]. These sites are identified from the literature data, and by the comparison of IR observation with MS measured ammonia TPD, solid acidities of four kinds of acid sites are measured individually.

IRMS-TPD experiment provides us with an interesting observation of the Brønsted acidity, because the IR observation shows the precise band position of the OH site. Therefore, it is the first time for us to study the solid acidity in a molecular level. With the IRMS-TPD experiment, the precise study of the Brønsted acidity became possible.

Density functional theory (DFT) calculation is also carried out to study the solid acidity in detail. DFT calculated value of energy of ammonia adsorption is easily compared with the experimentally determined value. It is our important advantage that both experimental observation and theoretical calculation are given and compared. Now, we have arrived at a highly advanced stage of the investigation of the solid acidity of zeolites.

DFT calculation is a powerful technique to learn the physical chemistry of zeolite acidity. Without the technique, we have no chance to study the significance of the zeolite acidity. ΔH values measured by the ammonia TPD was once confirmed by the comparison with the values measured by micro-calorimeter. However, there was no further chance to confirm the ΔH values measured by ammonia TPD. The advancement of theoretical understanding of the strength of acidity provides us with a chance to study the solid acidity in more detail. What an impressionable and surprising time we expe-

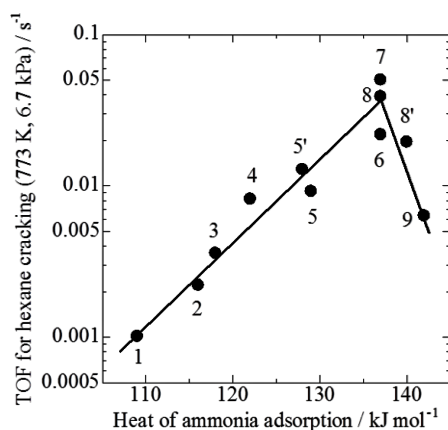


Fig. 6. Correlation between the TOF of hexane cracking at 773 K and the ΔH for ammonia adsorption on zeolites, H-Y (1), LaH-Y (2), BaH-Y (3), CaH-Y (4), ex-situ H- β (5), H- β (5'), H-ZSM-5 (6), EDTA-USY (7), ex-situ H-MCM-22 (8), H-MCM-22 (8'), and NaH-mordenite (9).

rienced, when we calculated the energy for ammonia desorption from the DFT; because the ΔH has been measured from the experiment of ammonia IRMS-TPD based on the derived equation, and also the energy for ammonia desorption is calculated from the quantum chemical theory; and both parameters agree well, as shown in Figure 4 [4].

2.4 Origin of the acidity strength and the cracking catalysis

Two important findings about the acidity are discussed. First topic is on the origin of the acidity. So often we have questions on the origin of the acidity. We stated that the strength is governed by the structure based on the experimental findings. DFT calculation gives us the value of energy as well as the precise parameter of the structure. Therefore, after the calculation, there are uncountable data of the structure of zeolite acidity which could be correlated with the energy parameter. Al-O bond distance and Si-O-Al angle are raised as key geometrical parameters to influence on the strength of acidity. However, precisely analysis of the structure and geometry tells us the strength of the acidity is correlated with both the distance and the angle between two neighbored triangles, as shown in Figure 5 [5]. This means that the compression by two neighbor triangles into the

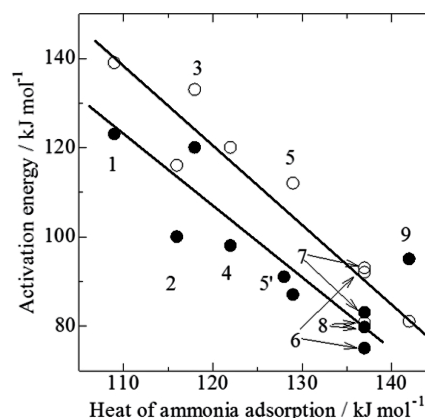


Fig. 7. Activation energy for the cracking of hexane (○) and octane (●) plotted against the ΔH on the zeolites, 1 to 9 referred to in Fig. 6.

cluster Si(OH)Al induces the strong Brønsted acidity. The compression to the Brønsted acidity from the surrounding triangle is estimated to be so weak in the meso-porous materials. In fact, the silico-alumino meso-porous materials do not show the strong acidity.

The most important and interesting observation is a relation between the catalytic activity and the solid acidity. Our interest is directed to understanding the activity for the cracking of alkane, octane and hexane. Our approaches to the understanding the catalysis are made by measuring turn-over frequency (TOF) and activation energy. The catalytic activity was measured by controlling the temperature and the partial pressure of alkane so that the mono-molecular reaction was measured. Number and strength of the Brønsted OH were measured in detail. When the multiple sites of the Brønsted OH exist, the accessible and active OH only is selected as active sites. Thus, TOF which is the rate divided by number of the active site is plotted against the ΔH , as shown in Figure 6 [6]. In the cracking of both octane and hexane, the volcano relationships were observed. In both cases, ZSM-5 and MCM-22 which have the ΔH about 135 to 140 kJ mol⁻¹ showed the maximum values. Activation energies of the cracking were measured, and these values are plotted against the ΔH as a parameter of acid strength in Figure 7. Activation energies decreased with increasing the strength of acid sites. However, the cracking of octane on NaH-mordenite (in Figure, shown 9) deviates strongly from the rela-

tionship. Further precise study is required to understand the relationship more profoundly. Thus, it will be so interesting to apply the combined technique to understanding the acidity and catalytic activity on various zeolites synthesized and modified by various methods.

3. CVD of silica

3.1 Intention of the modification and findings

Once I was asked, "Why did you try the modification of zeolites by silica? What did you expect from the experiment?" Unfortunately, I did not have a clear and noble intention. I just tried the modification with an intention of changing the catalyst property. I expected first that the alkoxide modified the zeolite totally. To say correctly, I expected that the acidity would be modified by the deposition. Actually, a technical term of chemical vapor deposition was not on our ideas. We understood that our modification would be included in one of the supporting methods of metal oxide. The term of chemical vapor deposition (CVD) was used in the publication of the communication in *Chem. Commun.*, when the Editor changed the title of the paper into a vapor-phase deposition method [7].

The first reagent I have used is silicon tetra-ethoxide $\text{Si}(\text{OC}_2\text{H}_5)_4$, which is usually abbreviated into TEOS. However, in the experiment using the reagent, the weight of catalyst did not increase as expected. I thought it was caused by molecular size largeness. And I looked for a smaller molecule, and found silicon tetra-methoxide $\text{Si}(\text{OCH}_3)_4$ in a catalogue of Shinetsu Silicon. In the next experiment using the silicon-methoxide, I found the increase of weight by the deposition enough to modify the material.

Two experiments were carried out after the modification. Actually, I asked Mr. H. Itoh who was a graduate student to do the experiments; ammonia TPD and methanol conversion were tested on the modified zeolite (mordenite). Ammonia TPD was not changed after the modification. However, product distribution in the methanol conversion changed dramatically. Benzene and toluene were the large molecules formed from the methanol conversion. It was not difficult to reply the question; *i.e.*, only the pore

size is enclosed without the modification of inside structure [8].

Adsorption of water and *o*-xylene on the modified zeolite gave us further clear and interesting findings. Because water and *o*-xylene had the molecular diameters of 0.26 and 0.63 nm, respectively, I studied the adsorption of small and large molecules. Adsorption of water was not changed at all after the modification, but the adsorption of *o*-xylene was suppressed greatly. The adsorption amount of *o*-xylene was so small, and it was expected due to the adsorption on the external surface.

3.2 Excellent shape selective reaction and adsorption

During the study on the CVD of silica, I encountered excellent findings three times; (1) selective cracking of linear alkane in preference to branched alkane on mordenite, (2) selective formation of *p*-xylene among xylene isomers as a result of toluene alkylation and disproportionation on ZSM-5, and (3) separation of oxygen and nitrogen on zeolite A. Among them, the most important study that drew people's attention is undoubtedly the *p*-xylene selective formation. *Para*-xylene is an important raw chemical compound to produce plastics and fiber, and produced by many industrial companies. The first observation was revealed by an experiment of methanol conversion on HZSM-5. Products in the reaction included various alkanes, olefins, and aromatics. Product distribution of the methanol conversion changed small by the deposition of silica; however the distribution of xylene isomers changed greatly, and *o*- and *m*-xylenes were not formed at all with *p*-xylene remained formed selectively at the deposition of silica [9]. Figure 8 shows the excellent shape selectivity to form *p*-xylene among xylene isomers from methanol conversion on the SiHZSM-5, reported in 1986.

Should the study be carried out nowadays, most probably, we would make a patent claim to not only domestic but also international communities. But, we did not have such a research circumstance at the time of 1986, and also we did not understand correctly the importance of the technique. It was 1991 when we published the selective formation of *p*-xylene in the alkylation and disproportionation of toluene [10]. Obviously, it was too late to claim our priority of the

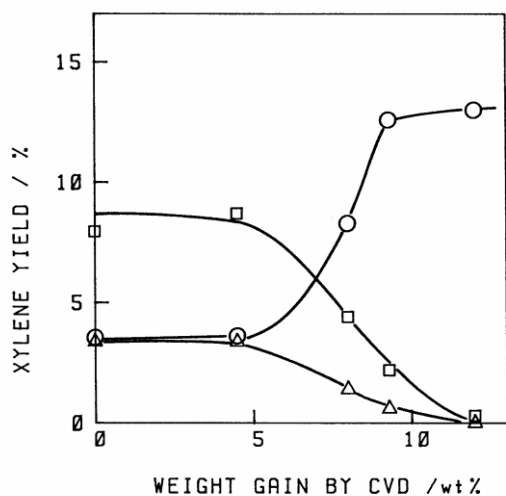


Fig. 8. Xylene isomers yields with increasing the amount of silica deposited on the HZSM-5. O- (Δ), m- (\square) and p- (\circ) xylenes were formed as a result of methanol conversion.

investigation. A similar study had already been published elsewhere. For example, Prof. Ikai Wang of National Taiwan University published the selective formation of *p*-xylene based on the silica modified HZSM-5. However, he visited us in Nagoya University before the publication, and then studied the CVD technique for their development of the selective catalytic process. (There was a group tour of research on the catalysis from Taiwan, and five to six researchers visited to Nagoya University.) He first proposed a method of *in situ* CVD method, where the extent of deposition was controlled by flowing methanol and toluene simultaneously with alkoxide in order to examine the degree of modification from the selectivity of *p*-xylene formation. This practical method first proposed by Wang was followed by Indian chemical industry and Prof. O' Connor of Cape town. Indian Petrochemicals led by Dr. Halgeri who is used to be a member of Ono laboratory of Tokyo Institute of Technology developed an industrial chemical process of *p*-diethylbenzene production. I guess that some other companies in the world utilized the CVD and a similar technique to develop the shape selective catalytic reaction, but it remained unopened yet.

3.3 Prospects in future study

This technique of silica CVD has been studied by many researchers in the world. On the other hand, similar techniques are studied recently for the development of the shape selective zeolite catalyst. One of them is chemical liquid deposition (CLD) using TEOS. Alkoxide is deposited on the zeolite in the liquid phase of such an organic solvent as heptane. Because of the organic solvent utilization, the temperature of CLD may be maintained at the temperatures lower than 373 K. The amount of deposited silica may be difficult to be correctly measured. Concept of the method is not different from that of CVD. However, fine and successful applications of the method have not seen before. Because I have not yet carried out the liquid phase deposition of silica, further comments on this method is difficult. However, I believe that the silica on the external surface of zeolite could be stabilized in a similar structure, when any kind of methods is adopted, as long as the process conditions are adequately controlled. Selection of the method to deposit the silica depends on the handling easiness and the required cost, *i.e.*, it depends on the economic balance of money and energy.

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